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PROCESS FOR THE SELECTIVE CATALYTIC HYDRODEALKYLATION OF
ALKYLAROMATIC HYDROCARBONS

The present invention relates to a process for the
10 catalytic hydrodealkylation of alkylaromatic hydrocarbons.

More specifically, the present invention relates to a
process for the catalytic hydrodealkylation of hydrocarbon
compositions comprising C₈-C₁₃ alkylaromatic compounds, op-
tionally in a mixture with C₄-C₉ aliphatic and
15 cycloaliphatic products.

Even more specifically, the present invention relates
to a process for the catalytic hydrodealkylation of
alkylaromatic hydrocarbons, in a mixture with aliphatic
products, wherein the reaction takes place in the presence
20 of water. The presence of water, together with the choice
of suitable operative conditions and catalyst formulation,
make the reaction, object of the invention, surprisingly
selective towards the hydrodealkylation of alkylaromatic
products, and efficient in quantitatively suppress-
25 ing transalkylation, isomerization, disproportioning and

condensation side-reactions.

This leads to a high yield in benzene, toluene and ethane (BTE) and reduced or non-formation of both methane and condensed products, essentially naphthalene and biphenyl products.

Processes for the catalytic conversion of alkylaromatic products are known in literature, wherein the addition of water under the process conditions, specifically promotes isomerization, disproportioning and transalkylation reactions, significantly jeopardizing the hydrodealkylation reaction, thus obtaining opposite results to those object of the present invention.

U.S. patent 4,431,857, for example, describes a catalytic process, carried out in the presence of a crystalline boron-silicate catalyst (AMS-1B) impregnated with molybdenum, wherein the addition of water, from 50 to 2000 ppm, to the feeding mix consisting of xylenes (ortho- meta- and para-) and ethylbenzene, causes their isomerization to para-xylene, thus inhibiting the direct dealkylation.

U.S. patent 5,773,679, describes a process for the catalytic conversion selectively directed towards the disproportioning reaction of toluene to para-xylene by the addition of water, in continuous or intermittently (from 0.01 to 10 ml*g/min), to the feeding mix, using a ZSM-5 zeolite treated with a silanizing agent. The ethylbenzene, ini-

tially present, and the heavier alkylaromatic products which are formed, however, do not undergo dealkylation under the reaction conditions.

U.S. patent 6,512,155 describes a sole isomerization
5 process carried out in the presence of water (from 75 to 750 ppm) in order to bring mixtures of xylenes, under non-equilibrium conditions, together with ethylbenzene, towards the selective production of p-xylene, so as to have a final equilibrium composition of xylenes. The reaction proceeds
10 in the presence of a zeolitic or non-zeolitic catalyst impregnated with Pt, and water is added in continuous or intermittently, as such or by means of an organic precursor (alcohol, ester, ether) capable of supplying it under the reaction conditions.

15 U.S. patent 6,500,997 describes a process for the conversion of C₇-C₁₀ alkylaromatic products via disproportioning/transalkylation, to obtain mainly xylenes, with an equilibrium composition, carried out on a catalyst based on mordenite or β -zeolite impregnated with bismuth. In this
20 case, the presence of water in the reaction is undesired, but the system guarantees, according to the invention, the maintenance of a high stability and activity even when water is present up to 500 ppm.

As far as the operative conditions and choice of catalyst are concerned, European patent 138,617 describes a
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process for the conversion of aromatic hydrocarbons by means of hydrodealkylation which comprises the treatment of a hydrocarbon stream, essentially consisting of ethylbenzene and xylenes, under conventional reaction conditions, with a zeolite catalyst modified with molybdenum. In the process described, the general reaction conditions do not allow a hydrodealkylation reaction without contemporaneous isomerization, transalkylation, disproportioning and condensation reactions. The limitations towards a selective catalytic hydrodealkylation also emerge from various other processes described in the known art. In some cases, this reaction even forms a side-reaction with respect to the isomerization, transalkylation, disproportioning and condensation reactions.

The Applicant has now unexpectedly found that it is possible to induce the catalytic hydrodealkylation reaction alone, in the presence of water, of C₈-C₁₃ alkylaromatic hydrocarbons to benzene, toluene and ethane (BTE), without contemporaneous isomerization, transalkylation, disproportioning and condensation reactions, by selecting suitable operative conditions and catalyst formulation.

In particular, the presence of water and the catalyst composition, both object of the present invention, have surprisingly allowed the selection of operative conditions so as to favour the hydrodealkylation alone of

alkylaromatic compounds. According to the process, object of the invention, not only is the hydrodealkylation reaction quantitatively selective towards the formation of benzene, toluene and ethane, with a reduced or null production of methane and condensed products (naphthalene and biphenyl derivatives), but the benzene/toluene ratio is always decidedly favorable towards benzene. The economical aspect of the process can therefore be referred to the intrinsic value of both the reaction streams: the liquid phase due to the remunerative value of benzene and toluene, with particular reference to benzene, always produced in larger quantities than toluene; the gaseous phase as a result of the possibility of recycling the ethane produced to any pyrolysis process, for example by recycling to ovens, with the considerable energy recovery guaranteed by this type of recycling.

An object of the present invention therefore relates to a process for the catalytic hydrodealkylation alone of hydrocarbon compositions comprising C_8-C_{13} alkylaromatic compounds, possibly mixed with C_4-C_9 aliphatic and cycloaliphatic products, which comprises the treatment, in continuous, in the presence of water, of said hydrocarbon compositions with a catalyst consisting of a ZSM-5 zeolite carrier having a molar ratio Si/Al of between 5 and 35, modified with at least one metal selected from those be-

longing to groups IIb, VIB and VIII, at a temperature ranging from 400 to 700°C, preferably between 450 and 600°C, a pressure ranging from 2 to 4 MPa, preferably between 2.8 and 3.6 MPa, a molar ratio between water and hydrocarbon charge ranging from 0.0006 to 0.16 (i.e. between 0.01 and 2.5% w/w), more preferably between 0.003 and 0.032 (i.e. between 0.05 and 0.5% w/w), a molar ratio H₂/charge of between 3 and 6, preferably between 3.8 and 5.2.

According to the present invention, the hydrocarbon charge which undergoes hydrodealkylation comprises C₈-C₁₃ alkylaromatic compounds, such as ethylbenzene, xylene, diethylbenzenes, ethylxylenes, trimethylbenzenes, tetramethylbenzenes, propylbenzenes, ethyltoluenes, propyltoluenes etc.. This charge can come, for example, from effluents of reforming units or units which effect pyrolytic processes, such as steam cracking, and can possibly contain a mix of C₄-C₉ aliphatic and cycloaliphatic products and organic compounds containing heteroatoms, such as, for example, sulfur, in the typical amounts generally present in charges deriving from reforming units or pyrolysis processes.

The hydrocarbon charge used in the present process can also be subjected to separation treatment, for example distillation or extraction, to concentrate the products which must subsequently undergo hydrodealkylation, or it can be

treated with aromatization processes to increase the concentration of alkylaromatic compounds and decrease the paraffin concentration. Furthermore, a previous hydrogenation of the charge may also be necessary, to eliminate the unsaturations present in the aliphatic compounds and on the same alkyl substituents of the aromatic rings. The same hydrogenation can remove sulfur, nitrogen or oxygen from the substances typically present in the charge to be treated, even if this latter aspect is not of particular importance as, under the catalytic hydrodealkylation conditions, according to the present invention, these heteroatoms are quantitatively removed (sulfur, for example, as H_2S).

The hydrodealkylation catalyst, according to the present invention, consists of a ZSM-5 zeolite modified with at least one metal selected from those of groups IIB, VIB and VIII. Molybdenum is preferred among the metals, object of the invention, used either singly or in pairs. The composition of the zeolite carrier is particularly important for the embodiment of the present invention, which comprises the hydrodealkylation of alkylaromatic compounds with the substantial absence of isomerization, transalkylation, disproportioning and condensation side-reactions. It has been verified that the use of a ZSM-5 zeolite with a high aluminum content, in particular having

Si/Al molar ratios of between 5 and 35, preferably between 15 and 30, contributes to obtaining the desired result.

ZSM-5 zeolites are available on the market or can be prepared according to the methods described in U.S. patents 5 3,702,886 and 4,139,600. The structure of ZSM-5 zeolites is described by Kokotailo et al. (Nature, Vol. 272, page 437, 1978) and by Koningsveld et al. (Acta Cryst. Vol. B43, page 127, 1987; Zeolites, vol. 10, page 235, 1990).

In the process of the present invention, the zeolite 10 catalyst is preferably used in bound form, adopting a binding compound capable giving it form and consistency, for example mechanical resistance, so that the zeolite catalyst/binder can be conveniently used in an industrial reactor. Examples of binders include aluminas, among which 15 pseudo-bohemite and γ -alumina; clays, among which kaolinite, vermiculite, attapulgite, smectites, montmorillonites; silica; alumino-silicates; titanium and zirconium oxides; combinations of two or more thereof, used such quantities as to have zeolite/binder weight ratios ranging from 100/1 20 to 1/10.

The dispersion of metals in the zeolite or zeolite/binder catalyst can be carried out according to conventional techniques, such as impregnation, ion exchange, vapor deposition, or surface adsorption. The incipient im- 25 pregnation technique is preferably used, with an aqueous or

aqueous-organic solution (the organic solvent being preferably selected from alcohols, ketones and nitriles or mixtures thereof), containing at least one hydro- and/or organo-soluble of the metal, with a final total content of the metal in the catalyst ranging from 0.5 to 10% by weight.

The zeolite, with or without a binder, is subjected to impregnation with a metal of groups IIB, VIB and VIII, in particular, molybdenum.

10 The bound or non-bound catalyst can be treated according to methods which include:

- preparing one or more solutions of compounds of the metals to be carried;
- impregnating the zeolite with the above solutions;
- 15 - drying the zeolite thus impregnated:
- calcining the zeolite, impregnated and dried, at temperatures of between 400 and 650°C;

possibly repeating the above steps several times, according to necessity.

20 Examples of compounds of the metals used are: molybdenum(II) acetate, ammonium(VI) molybdate, diammonium(III) dimolybdate, ammonium(VI) heptamolybdate, ammonium(VI) phosphomolybdate and analogous salts of sodium and potassium, molybdenum(III) bromide, molybdenum(III)-(V) chloride, molybdenum(VI) fluoride, molybdenum(VI) oxychloride,

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molybdenum(IV)-(VI) sulfide, molybdic acid and the corresponding acidic salts of ammonium, sodium and potassium, and molybdenum(II-VI) oxides.

At the end of the impregnation, the total metal content, alone or in pairs, in the catalyst ranges from 0.1 to 10% by weight, preferably from 0.5 to 8% by weight.

Once the preparation of the catalyst has been completed, the same is charged into a fixed-bed reactor, fed in continuous with the hydrocarbon charge, hydrogen and water. The water is fed, according to convenience, either already vaporized, so that it can be mixed directly with the hydrocarbon charge, previously brought to gas phase, or by the addition of a carrier compound, miscible with the liquid charge, capable of releasing it under the reaction conditions.

Among compounds miscible with the liquid hydrocarbon charge, alcohols, ethers and esters can be used. Alcohols are preferred, and among these ethanol or phenethyl alcohol. For example, ethyl alcohol releases the water desired and ethylene, under the reaction conditions. The latter is immediately hydrogenated to ethane, adding it to the amount present in the gas phase selectively produced by the hydrodealkylation reaction.

Among the fundamental experimental parameters, the selection of the flow rate of the reagents is of vital importance.

tance in order to obtain a selective hydrodealkylation of the C₈-C₁₃ aromatic hydrocarbons possibly in a mixture with C₄-C₉ aliphatic and cycloaliphatic hydrocarbons. The feeding rates of the hydrocarbon, water and hydrogen mix, or of the carrier compound, must therefore be such as to guarantee an LSHV (Liquid Hourly Space Velocity), calculated on the hydrocarbon stream, ranging from 3 to 5 h⁻¹ and, more preferably, between 3.5 and 4.5 h⁻¹.

For this purpose, the molar ratio between hydrogen and the charge fed to the reactor must remain within the range of 3 to 6 mol/mol, more preferably between 3.8 and 5.2 mol/mol. In particular, the molar ratio between the water and hydrocarbon charge fed to the reactor is between 0.0006 and 0.16 (i.e. between 0.01 and 2.5% w/w), more preferably between 0.003 and 0.032 (i.e. between 0.05 and 0.5% w/w).

The experimental apparatus for the reaction includes a stainless steel fixed-bed reactor with an internal diameter of 20 mm and a total height of 84.5 cm, an electric heating device surrounding the reactor, a cooling system, a gas-liquid separator and a liquid high pressure pump.

The isothermal section of the reactor, maintained at a constant temperature by automatic control, is charged with the catalyst. The remaining reactor volume is filled with an inert solid in granules, for example, corundum, in order to guarantee an optimal distribution and mixing of the

gaseous reagent flow before the catalytic bed and the heat supplied to the reaction.

A pre-heater, positioned before the reactor, which operates at a temperature ranging from 200 to 400°C, more preferably between 250 and 320°C, contributes to the optimal contact of the reagents in gaseous phase (hydrocarbon mix, water and hydrogen) with the catalyst. This system favours the establishment of isothermal conditions in very rapid times, not only limited to the fixed-bed, but also along the whole reactor, allowing an easier and more accurate control of the operating temperature of the catalyst. The liquid and gaseous effluents produced by the reaction are separated and analyzed via gas chromatography, at intervals.

The following examples provide a further illustration of the process according to the present invention and should in no way be interpreted as limiting its scope as indicated in the enclosed claims.

REFERENCE EXAMPLE FOR THE CATALYST PREPARATION

20 Catalyst A (comparison)

A catalyst A is prepared, obtained by mixing a ZSM-5 zeolite and an alumina as binder, the two phases being in a weight ratio of 60/40, and extruding the mixture.

The extruded product is calcined in air at 550°C for 5 hours and its surface area BET is 290 m²/g.

Once at room temperature, the above is crushed and sieved to produce a powder having dimensions of between 20 and 40 mesh (between 0.84 mm and 0.42 mm), so that 12.4 g of catalyst powder have an equivalent volume of 20 ml.

5 Catalyst B

Catalyst B is obtained by impregnating catalyst A (50 g) with an aqueous solution (60 ml) containing 1.88 g of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ at about 25°C for 16 hours, and is subsequently placed under a nitrogen flow for
10 12 hours, dried in an oven at 120°C for 4 hours under vacuum and calcined in air at 550°C for 5 hours. The calculated molybdenum content is 2.0% by weight, against the value of 2.1% by weight determined by means of ICP-MS analysis.

15 EXAMPLES 1-9

The reactor is charged with 20 cm³ (12.4 g) of catalyst A, whereas the remaining volume is filled with granules of corundum to guarantee the optimal distribution and mixing of the gaseous flow of the reagents and of the heat
20 supplied to the reaction.

The hydrocarbon charges, whose compositions are indicated in Table 1, are fed to the reactor suitably mixed with hydrogen. The aliphatic fraction in the charge consists of C₄-C₉ products and the saturated C₅ indane ring.
25 The ethanol present in Charge 2 in an amount of 5% w/w sup-

plies a quantity of equivalent water of 1.95% w/w.

Table 1 - Composition of the feeding charge

Charge type	Charge 1	Charge 2
Concentration	weight %	weight %
Ethanol (H ₂ O as carrier)	--	5
Ethylbenzene	34	32.3
o, m, p-xylene	32	30.4
Indane	9	8.6
Cumene	1	0.9
n-propylbenzene	3	2.9
2-, 3-, 4-ethyltoluene	16	15.2
Σ (C ₄ -C ₉ Aliph. + C ₉ + Arom.)	5	4.7
Total	100	100

The reaction is carried out at a pressure of 3 MPa with a flow-rate of the reagent charge which is such as to have an LHSV of 3.9-4.1 h⁻¹, and a molar ratio H₂/charge of 4.2-4.4. The results are indicated in the following table 2.

Table 2

Example	1	2	3	4	5	6	7	8
Reaction temperature	510 °C	510 °C	510 °C	510 °C	550 °C	550 °C	550 °C	550 °C
Catalyst	A	A	B	B	A	A	B	B
Charge	1	2	1	2	1	2	1	2
Charge conversion (%)	78.6	76.4	84.5	80.9	81.3	76.1	88.7	81.8
Liquid effluent composition	weight %	weight %	weight %	weight %	weight %	weight %	weight %	weight %
Methane	10.3	2.6	3.2	1.0	13.8	2.7	7.0	1.5
Ethane (E)	11.2	6.8	20.6	14.8	11.4	9.7	19.2	15.4
Σ C3	3.1	7.8	3.8	3.3	1.3	7.5	2.2	2.5
Σ C4-C5	...	0.2	0.1	0.1	...	0.2	0.1	0.1
Ethyl benzene	0.9	2.8	0.2	1.0	0.8	3.5	0.1	0.6
o, m, p-xylene	15.9	20.2	13.1	16.4	14.5	21.3	10.0	15.5
Indane
Cumene
Σ C9-C9+ Aromatic compounds	5.5	4.2	3.0	3.3	5.0	2.4	1.9	2.4
Benzene (B)	24.0	29.2	27.2	33.8	26.3	26.9	29.6	35.1
Toluene (T)	28.4	26.2	28.8	26.3	26.9	25.8	29.9	26.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Σ BT	52.4	55.4	56.0	60.1	53.3	52.7	59.5	62.0
Selectivity to BT	66.7	72.5	66.3	74.3	65.6	69.3	67.1	75.8
Σ BTE	63.9	62.2	76.6	74.9	64.7	62.4	78.7	77.4
Selectivity to BTE	80.9	81.4	90.6	92.6	79.6	82.0	88.7	94.6
R(B/T)	0.76	1.12	0.94	1.29	0.98	1.04	0.99	1.31
R(BE/T)	1.24	1.37	1.66	1.85	1.40	1.42	1.63	1.88

Table 3

Example	4	8	9
Reaction temperature	510 °C	550 °C	585 °C
Catalyst	B	B	B
Charge	2	2	2
Charge conversion (%)	80.9	81.8	86.1
Liquid effluent composition	weight %	weight %	weight %
Methane	1.0	1.5	1.6
Ethane (E)	14.8	15.4	16.1
Σ C3	3.3	2.5	1.8
Σ C4-C5	0.1	0.1	0.1
Ethyl benzene	1.0	0.6	0.4
o, m, p-xylene	16.4	15.5	11.3
Indane
Cumene
Σ C9-C9+ Aromatic compounds	3.3	2.4	1.8
Benzene (B)	33.8	35.1	37.5
Toluene (T)	26.3	26.9	29.0
Total	100.0	100.0	100.0
Σ BT	60.1	62.0	66.5
Selectivity to BT	74.3	75.8	77.2
Σ BTE	74.9	77.4	82.6
Selectivity to BTE	92.6	94.6	95.9
R(B/T)	1.29	1.31	1.29
R(BE/T)	1.85	1.88	1.85

Under the same operating conditions, it can be observed (see Table 2, Examples 1-8) how, both at 510 and 550°C, the selectivity of the hydrodealkylation reaction to Benzene plus Toluene (BT, liquid phase) or to Benzene plus Toluene plus Ethane (BTE, liquid phase and gas phase) is always the highest when the ZSM-5/Mo catalytic system is operating in the presence of H₂O (Examples 4 and 8).

The B/T and BE/T ratios which can be considered as "main indexes" of the hydrodealkylation selectivity, give an immediate vision of this positive trend.

Table 3 (Examples 4, 5 and 9) and Figure 1 enclosed, show how, under the same overall operating conditions, the temperature rise to 585°C (Example 9) allows the conversion of the charge to be increased to values typical of tests with molybdenum alone. This conversion recovery is obtained as a result of a significant reduction in the residual concentration of xylenes and heavier aromatics (C₉-C₉₊). The quantity of xylenes and higher aromatic products converted per single passage is such as to sustain their recycling to the reactor affluent.

The concentration of methane deriving from the hydrogenolysis of the aromatic ring (generally favoured at the highest temperatures), does not change significantly and in the tests with H₂O, it always remains substantially lower than that obtained with molybdenum alone. Further-

more, the contemporaneous reduction in heavier aromatic products (C_9 - C_{9+}) minimizes the possibility of the formation of condensation side-reactions (also generally favoured at the highest temperatures) which create polycondensed aromatic products and coke which deactivate the catalyst.

All these results indicate the unexpected existence of an extremely strong synergy between the catalyst and H_2O to the extent that the overall ZSM-5/Mo/ H_2O system should be considered as being the real reaction catalyst. The results relating to the conversion and selectivity and consequently also to the activity, indicate a surprising stability of the catalytic system with respect to degradation effects due to the presence of water also at high temperatures, unlike what is described in the known art.